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Lithium-air Battery: Study of Rechargeability and Scalability

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Abstract:

Lithium-air battery is anticipated as the battery with highest energy density among all existing rechargeable battery systems known now. Literature reports suggest that the theoretical energy density of Li-air battery is close to that of gasoline. Thus, if successfully developed, rechargeable Li-air battery will be a suitable substitute for gasoline for electric vehicles. The research and development work is at initial stages worldwide at present. Electrochemistry of oxygen in non-aqueous electrolytes is one of the crucial factors. Development of a suitable catalyst for reversible oxygen electrode for long cycle-life is important. The research and development work available in the literature and also in the investigator's laboratory is based on small experimental

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14. ABSTRACT
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15. SUBJECT TERMS
Batteries, lithium-air battery, Rechargeability, Scalability

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Introduction:

In Li-air battery, Li metal is stored within the cell and oxygen is consumed from air. The cell functions in a non-aqueous electrolyte by oxidation of Li metal to Li$^+$ ion and oxygen absorbed from air undergoes reduction to superoxide, peroxide or oxide. The corresponding electrochemical reactions are given below.

At the anode, $Li \longrightarrow Li^+ + e^-$

At the cathode, $O_2 + Li^+ + e^- \longrightarrow LiO_2$ (lithium superoxide)

$LiO_2 + Li^+ + e^- \longrightarrow Li_2O_2$ (lithium peroxide)

$Li_2O_2 + Li^+ + 2e^- \longrightarrow Li_2O$ (lithium oxide)

The electrochemical properties of the oxygen electrode largely influence the performance of Li-air cells. Carbon is usually used as the substrate for oxygen reaction. The physical structure of carbon such as surface area, porosity, wettability, etc., and the catalyst influence electrochemistry of reversible oxygen electrode reaction. After screening several carbon samples, it is found that an activated carbon sample purchased from China has surface area as high as 1500 m^2/g and the performance of air – electrodes made of this carbon is good. Several

experiments are performed using this carbon. Cells made of 40 mm diameter are found to function well and several experiments are conducted to achieve rechargeability.

Detailed description of the project with analytical/experimental work:

Cells are machined out of Teflon. Various components of cells of 40 mm and 10 mm diameter are shown in Figure 1, and assembled cells are shown in Figure 2. For preparation of air electrodes, carbon powder and a binder (Teflon suspension (PTFE) or polyvinyledene fluoride (PVDF)] are mixed together and subjected to grinding thoroughly. In the case of PTFE binder, the powder becomes a dough which was rolled into a thin sheet. In the case of PVDF, a few drops of solvent, n-methyl pyrrolidinone (NMP) are added to get a syrup. Ni mesh of 12 mm diameter is sectioned out of a sheet of mesh, etched in dil-H_2SO_4 and dried. Carbon mixed with binder is applied on Ni mesh, pressed under hydraulic press, and dried. Cells are assembled in argon filled glove box employing lithium foil as the anode and 1.0M $LiPF_6$ dissolved in propylene carbonate as the electrolyte. Cells are taken out of the glove box and an oxygen filled bulb is connected to carbon electrode. Cells are allowed to rest for about three hours and then subjected to charge-discharge cycling by passing a constant current through the cell. Discharge capacity values are calculated in the units of mAh/g. The mass of carbon is used for calculation of specific discharge capacity.

Results and discussion:

(A) Studies with large are electrodes: Nickel gauge of 40 mm diameter was used as the current collector. Active layer consisting of the China carbon and α-MnO_2 catalyst was applied on one side and diffusion layer consisting of only carbon was applied on the other side. The sandwich was compacted under hydraulic press Li foil of 40 mm diameter was sectioned out of Li ribbon and Li-oxygen cell was assembled using a porous absorbing glass membrane separator soaked in

the electrolyte consisting of propylene carbonate and $LiPF_6$ (1M). The cells were discharged with 2 mA current. As the discharge rate was slow, current was increased to 5 mA. The variation of cell voltage with time is shown in Figure 3. A discharge capacity of 910 mAh/g is obtained. After the first discharge, the cells were subjected to charging. There was no charge pickup. When done repeatedly for 10 charge-discharge cycles, the discharge capacity was almost nil from the second cycle onwards (Figure 4). The discharge capacity obtained from the large area electrodes is high.

(B) Studies of various catalysts for rechargeability

(1) α-MnO_2 nanowires:

MnO_2 nanowires were prepared by hydrothermal method. In a typical procedure, an aqueous solution of $KMnO_4$ (0.5 g $KMnO_4$ in 60 ml DD water) was transferred into a PTFE lined stainless steel autoclave and held at 180°C for 24 h. After that it was allowed to cool down to room temperature. Then final product was centrifuged and dried at 80°C in oven. This material was tested as a catalyst for Li-air cell. The cells were assembled in argon atmosphere glove box. Variation of specific capacity with cycle number shown in Figure 5.

(2) α-MnO_2 by sonochemical method:

α-MnO_2 was synthesized by sonochemical method. In this experiment, 1.267 g of $MnSO_4$ was dissolved in 50 ml of water and gradually transferred to the beaker containing 0.79 g of $KMnO_4$ dissolved in 50 ml. The reaction mixture was mixed by ultrasonication for 30 minutes at 30 Amp. The product was centrifuged and dried in vacuum around 50°C.

$$KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow MnO_2 + K_2SO_4 + 2 H_2SO_4$$
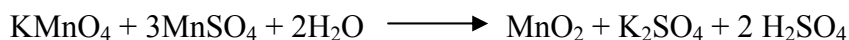
Air electrode was made using this α-MnO$_2$, which was supported on China carbon. Figure 6 shows the variation of specific capacity versus cycle number. Initially, the specific capacity is about 400 mAh/g, and it is low in subsequent cycles.

(3) α-MnO$_2$ by precipitation method:

α-MnO$_2$ was prepared by precipitation method. In a typical procedure, 0.15 M MnSO$_4$ was added drop wise to the beaker containing 0.1 M KMnO$_4$. Then the solution was kept under stirring for 4-hours and final product was centrifuged and tried in oven at 80°C.

(4) α-MnO$_2$ and China carbon composite:

α-MnO$_2$ was synthesized on the surface of China carbon by insitu method. In this experiment, a solution of KMnO$_4$ (18 mg in 20 ml of water) was prepared and 200 mg of carbon was dispersed in it. The mixture was stirred thoroughly. Then, a solution containing MnSO$_4$ (40 mg in 10 ml) was added drop wise and stirred for 2 h. The product was centrifuged and washed thoroughly with water then dried at 50°C in oven. Electrodes were prepared using this composite and assembled in glove box. The cell gave 15 cycles of rechargeability with low capacity between 70 – 200 mAh/g (Figure 7).

(5) Vulcan carbon and α-MnO$_2$:

Vulcan carbon was tried as a supporting material in the place of China carbon. Two swagelok cells were assembled using α-MnO$_2$ catalyst. It gave good cyclability for about 20 cycles, but with low capacity (Figure. 8). Different Wt % of catalyst MnO$_2$ (2.5, 5, 10, and 15 %) did not produce better results.

(6) Polyaniline and China carbon:

Conducting polymer polyaniline was prepared by oxidative polymerization of aniline using ammonium per-sulfate as an oxidizing agent in acidic medium. In a typical procedure, 5 ml of aniline was dissolved in 100 ml of 1 M H_2SO_4 acid. Then the solution was cooled to about 5 - 10°C stirred for 30-min and the 5 Wt % of ammonium persulfate $[(NH_4)_2S_2O_8]$ added drop wise. Blue-greenish precipitate was obtained. The final product was centrifuged and washed several times with dil. H_2SO_4.

Polyaniline was tried as a catalyst for Li-O_2 cell. The capacity of cell with polyaniline was only about 600 mAh/g in the first cycle (Figure 9). It exhibited rechargeability for about 6 charge-discharge cycles, but with decreased capacity. A combination of polyaniline and α-MnO_2 as catalyst mixture provided 5500 mAh/g initially, but there was no rechargeability (Figure 10).

(7) Li_2O and Li_2O_2 mixture as active material:

Cells were assembled by using Li_2O and Li_2O_2 (25 % each) as active material along with α-MnO_2 (4.85 %) (prepared by precipitation method) catalyst and China carbon (19 %) support. Initially, the discharge capacity was 450 mAh/g. In subsequent cycles, a capacity of about 50 mAh/g is obtained for about 20 cycles (Figure 11). Thereafter the cell did not pick up charge.

(8) Ni - MnO_2 composite as a catalyst:

Ni - MnO$_2$ composite was prepared by insitu method. 132 mg of NiCl$_2$.6H$_2$O (required to obtain 50 mg of Ni) was dissolved in minimum amount of water. Another solution consisting of 143 mg of KMnO$_4$ (required to get 50 mg of MnO$_2$) was prepared in minimum amount of water. Both solution were stirred for 15-min before adding NaBH$_4$ reducing agent (130 mg). The color of the solution turned to black-brown at the end of the reaction. By using this material as a catalyst (5 wt %), electrodes were made on Vulcan carbon support. A discharge capacity of about 1260 mAh/g was obtained, and there was no rechargeability (Figure 12).

(9) LiMn$_2$O$_4$ as a catalyst:

LiMn$_2$O$_4$ was tried as a catalyst and China carbon as support. Cells were assembled using electrodes made by this material. Specific capacity 993 mAh/g was obtained (Figure 13) with no rechargeability.

(10) Cobalt phosphate as catalyst:

Cobalt phosphate was tried as a catalyst, because it was reported that it can acts as a good electrocatalysts on water splitting. It was prepared by precipitation method and electrodes were made using 5 % Cobalt phosphate as the catalyst and assembled in swagelock cell. LiPF$_6$ dissolved in propylene carbonate and diethylene carbonate was used as the electrolyte. The first discharge capacity was 2250 mAh/g, and faded fast but without rechargeability (Figure 14).

(11) Ceria as a catalyst:

CeO$_2$ nanoparticles were tried as a catalyst. The non-stoichiometric oxygen distribution in its lattices and application as reducing agent as catalytic convertor prompted to study this material as a catalyst for oxygen reduction and oxygen evolution in Li-O$_2$ cell. It was prepared by precipitation method, in which cerium source precipitated as cerium oxalate and subsequent calcinations yield CeO$_2$ nanoparticles. In a typical procedure, 0.15 M cerous nitrate solution was added drop wise to 1.5 M ammonium oxalate under stirring and the mixture was kept at 70°C for about one hour. Final a white color (cerium oxalate) formed. The precipitate was centrifuged and washed with water several times. This cerium oxalate was calcined at 700°C for 2 hours under oxygen atmosphere. The capacity obtained from Li-O$_2$ cells assembled using CeO$_2$ as the catalyst was very low (Figure 15).

(12) China carbon and Ni powder composite:

Nickel (5 %) and China carbon composite was prepared insitu by simple chemical reduction method using sodium borohydride as the reducing agent. 50 mg of NiCl$_2$.6H$_2$O was dissolved in 10 ml of water and then 250 mg carbon was dispersed. The mixture was stirred thoroughly to attain homogeneous mixture. Then, solution containing sodium borohydride (25 mg in minimum amount of water) was added drop wise. After allowed these mixtures for two hours under stirring, product was centrifuged and washed thoroughly with water then dried at 50°C in oven. Swagelok cell was assembled using this material. It gave first discharge capacity of 1217 mAh/g (Figure 16). There is no rechargeability.

(13) Ag/China carbon composite:

200 mg of China carbon was dispersed in 20 ml water and stirred for an hour. The 10 ml of AgNO$_3$ (36 mg) was added to the dispersion and sodium borohydride was added drop wise. Then the resulting mixture was centrifuged and dried at 50°C. This Ag/China carbon material was used as an active material. Electrodes were made and assembled in swagelock cells. It gave high capacity 4701 mAh/g but there was no rechargeability (Figure 17).

(14) TiO$_2$ nanotube:

TiO$_2$ nanotubes were studied as a catalyst; it was prepared by hydrothermal method. Cell was assembled in swagelock. A discharge capacity of about 1350 mAh/g was obtained in the first cycle and thereafter there was no rechargeability (Figure 18).

(15) Pyrogallol as a catalyst:

Pyrogallol was tried as a catalyst as it has properties of absorbing oxygen. In this experiment pyrogallol (commercial) used along with α-MnO$_2$ as catalyst. Cell was assembled in Teflon. It gave good cyclability upto 10 cycles (Figure 19). The discharge capacity decreased gradually (Figure 19).

(16) Benzoquinone as a catalyst:

Benzoquinone was attempted as catalyst for Li-air cell. It was investigated along with α-MnO$_2$. Cell was assembled in Teflon. The second cycle discharge capacity was high, but it decreased on further cycling (Figure 20).

(18) Li$_2$Pc and China carbon:

Li$_2$Pc was tested as a catalyst for oxygen reduction and the results are published in Journal of Porphyrins and Phthalocyanines. This paper is attached. The journal highlighted this work as cover page.

(19) Ionic liquids:

Ionic liquid (N-propyl-N-methyl pyrrolidinium bis (trifluoromethane sulfonyl imide)) were used as a solvent for electrolyte. Electrodes were prepared using China carbon and MnO$_2$. The cell gave very low capacity but there was reversibility (Figure 21).

(20) Ether solvent, TEGDME:

TEGDME was tested as solvent for electrolyte in Li-Air cell. It was found that it gave good reversibility for a few cycles but with low capacity (Figure 22).
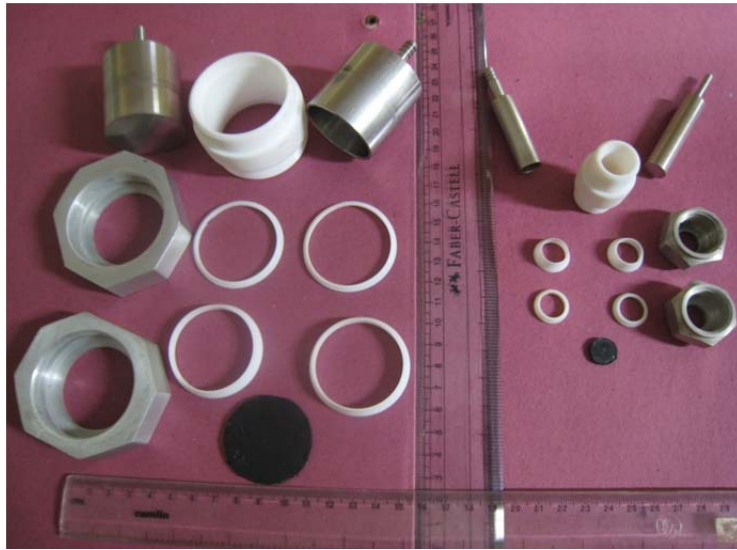
Fig 1: Various parts of swagelock cells including electrodes
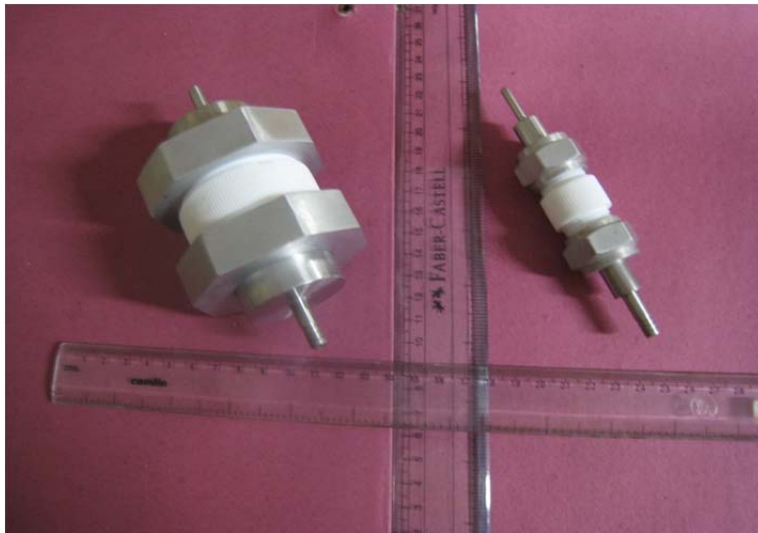
Fig 2: Assembled Swagelock cells big and small
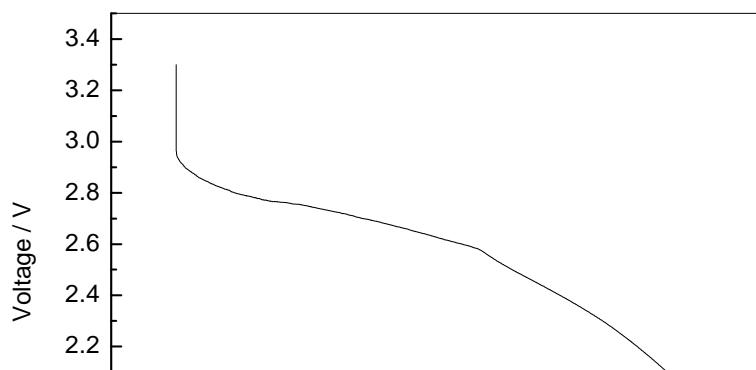
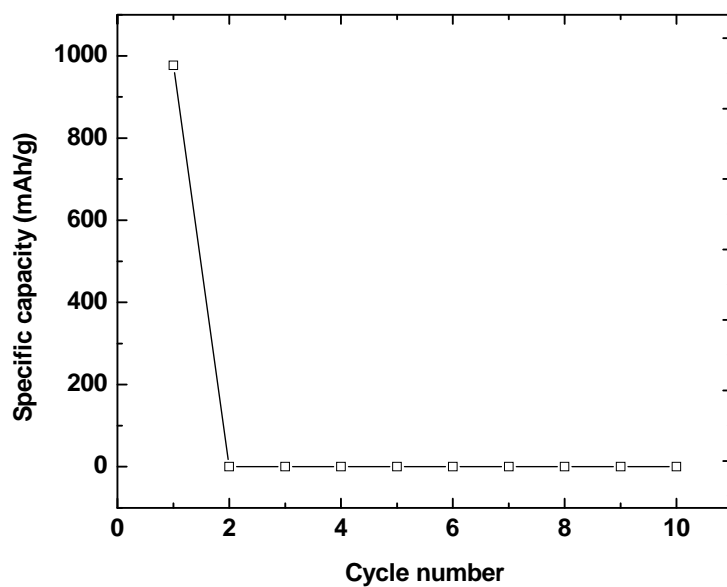Fig 3: Discharge voltage profile curve of Li-air cell with 0.2 mA current

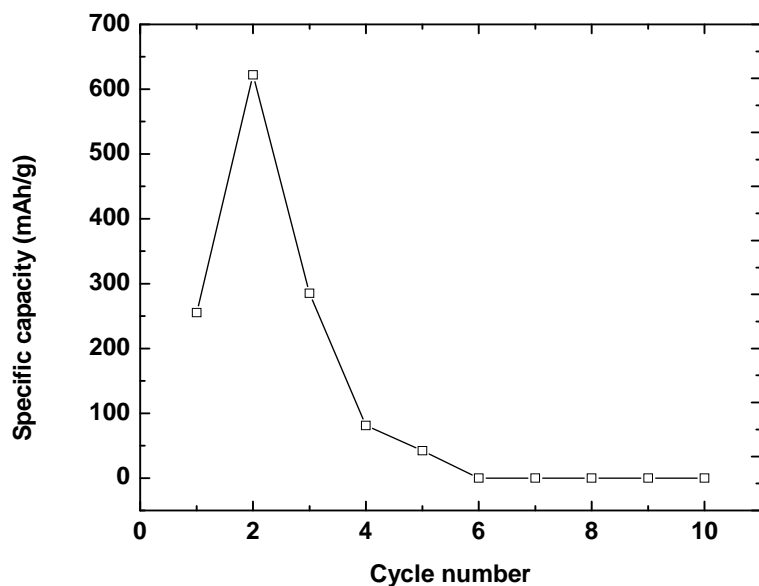Fig 4: Specific capacity versus cycle number of Li-air cell discharged at 2 mA

Fig 5: Specific capacity versus cycle number of a Li-air cell employing MnO_2 nanowires as a catalyst. Cell area: 1.1 cm^2 and cell current: 0.2 mA.
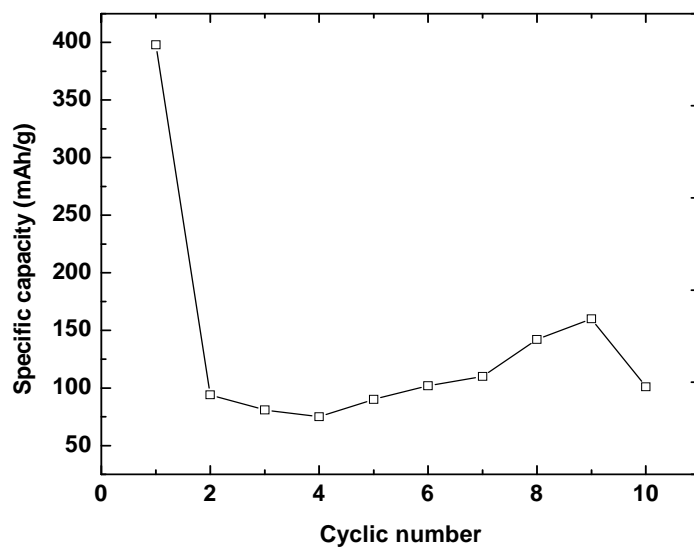

Fig 6: Specific capacity versus cycle number of Li-air cells with α-MnO_2, synthesized by sonochemical method as a catalyst. Cell area: 1.1 cm^2 and current: 0.2 mA
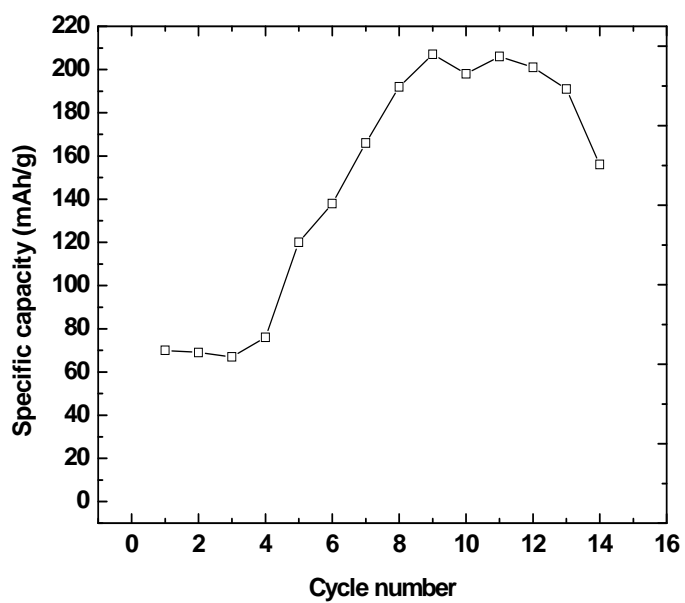
Fig 7: Specific capacity versus cycle number of a Li-air cell with China carbon - MnO_2 composite as the active material. Cell area: 1.1 cm^2 and current: 0.2 mA

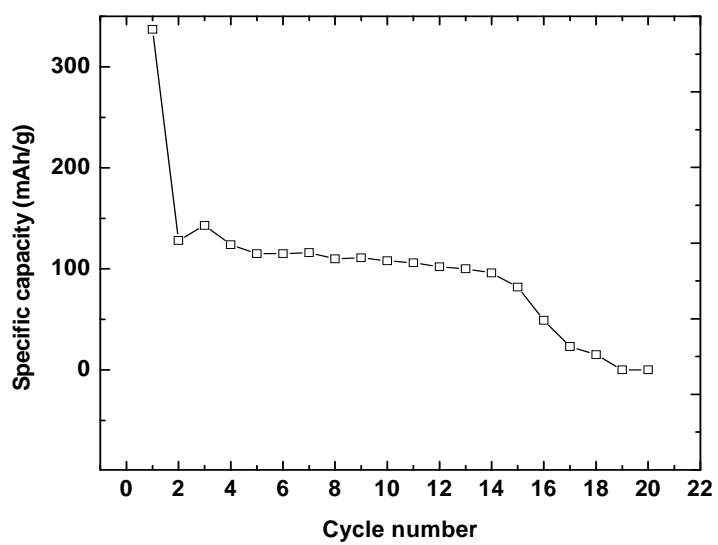
Fig 8: Specific capacity versus cycle number of a Li-air cells with Vulcan carbon - MnO_2 composite as the active material. Cell area: 1.1 cm^2 and current: 0.2 mA
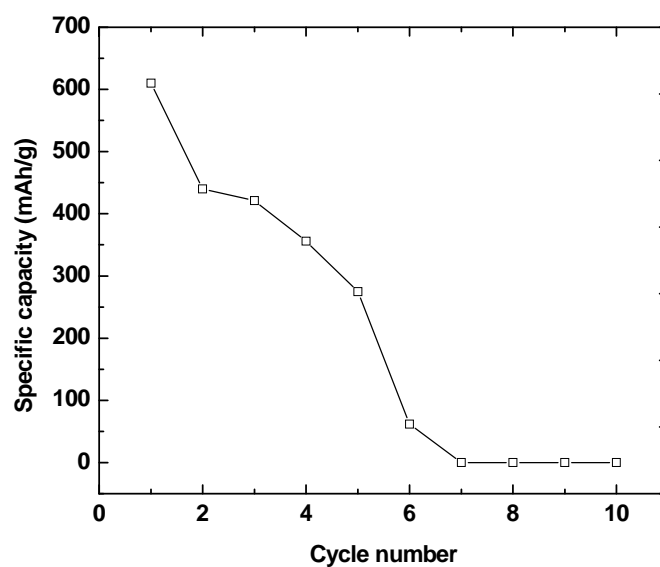
Fig 9: Specific capacity versus cycle number of Li-air cell with polyaniline and China carbon composite as the active material. Cell area: 1.1 cm^2 and current: 0.2 mA
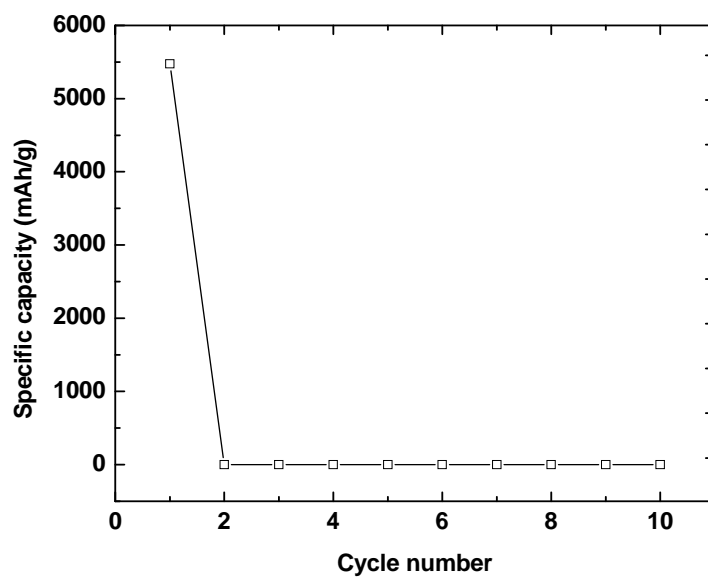

Fig 10: Specific capacity versus cycle number of a Li-air cell tested with polyaniline and MnO$_2$ as a catalyst. Cell area: 1.1 cm^2 and current: 0.2 mA

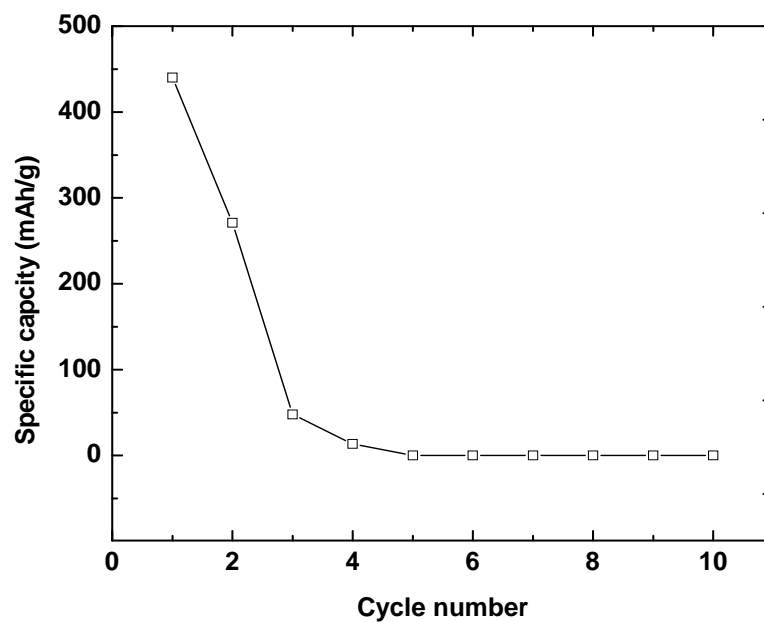Fig 11: Li$_2$O and Li$_2$O$_2$ mixture was studied as active material and MnO$_2$ (prepared by precipitation method) as the catalyst. The graph shows specific capacity versus cycle number of a cell cycled at 0.2 mA. Cell area: 1.1 cm^2
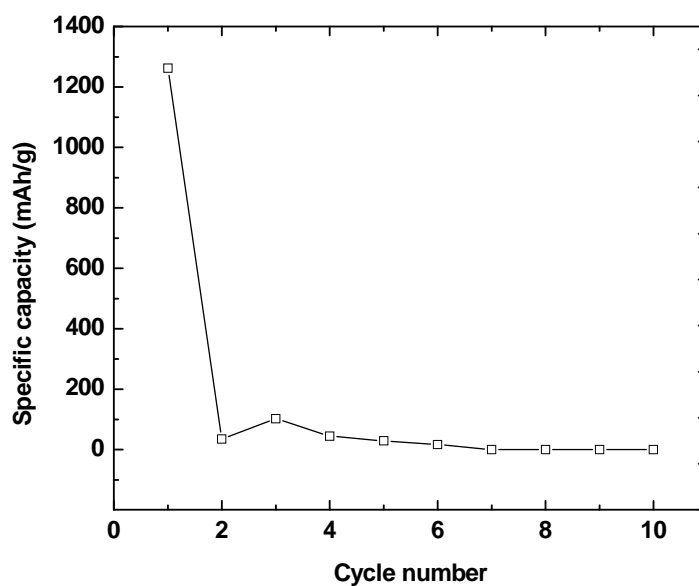

Fig 12: Specific capacity versus cycle number for cell with oxygen electrode made of Ni - MnO$_2$ catalyst on Vulcan carbon support. Cell area: 1.1 cm^2 and current 0.2 mA
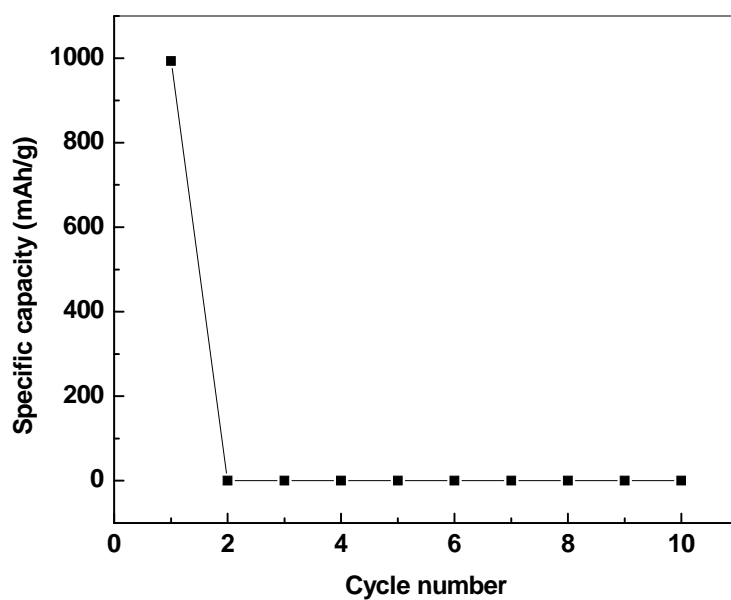
Fig 13: Variation of specific capacity with cycle number of Li-O$_2$ cell employing LiMn$_2$O$_4$ catalyst on China carbon support. Cell area: 1.1 cm^2 and current: 0.2 mA
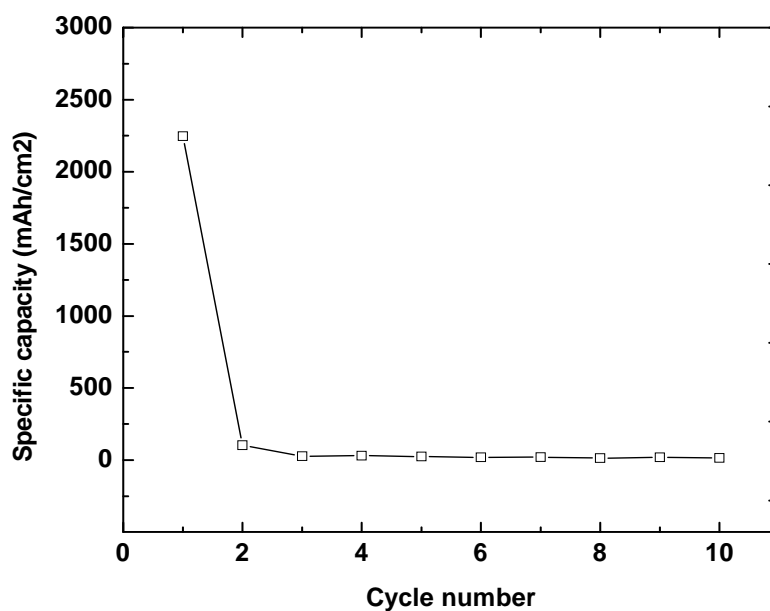
Fig 14: Variation of specific capacity with cycle number of Li - O$_2$ cell employing cobalt phosphate catalyst on China carbon support. Cell area: 1.1 cm^2 and current 0.2 mA
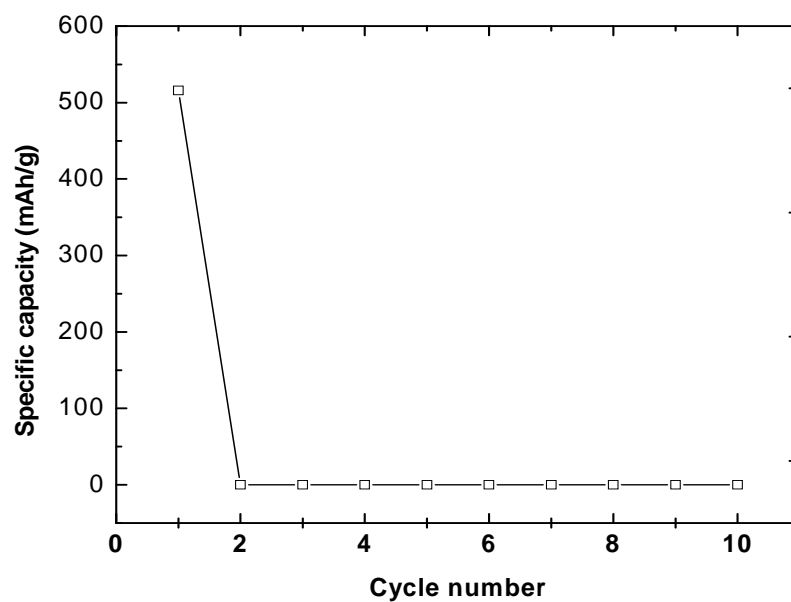
Fig 15: Variation of specific capacity with cycle number for ceria catalyst on china carbon. Cell area: 1.1 cm^2 and current: 0.2 mA
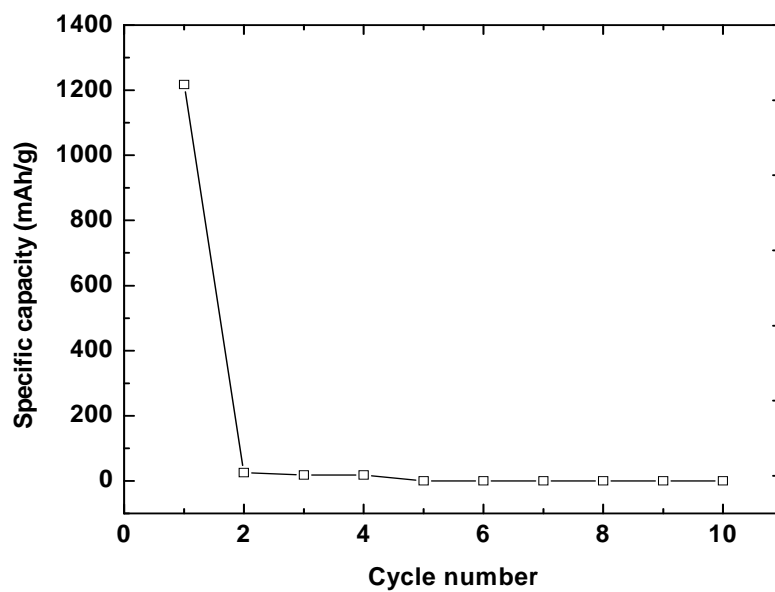
Fig 16: Specific capacity versus cycle number for the cell with nickel powder as catalyst on China carbon support. Cell area: 1.1 cm^2 and current: 0.2 mA
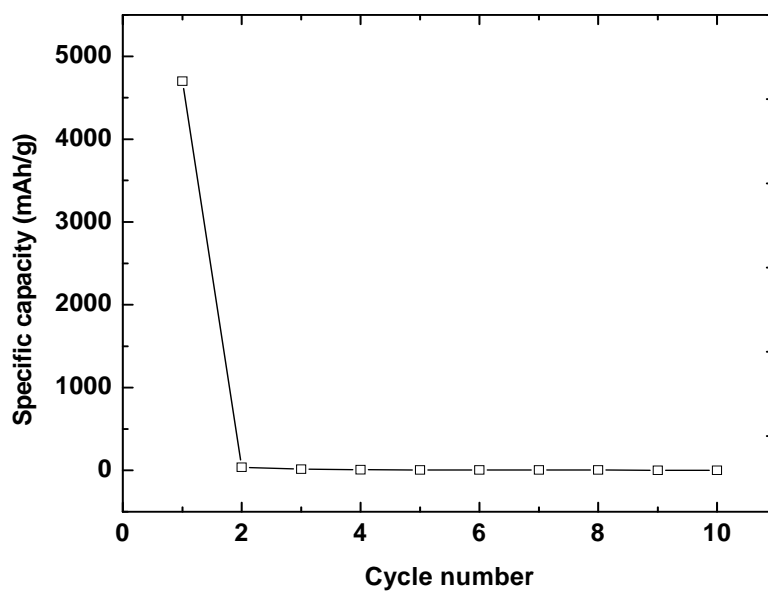
Fig 17: Variation of specific capacity with cycle number of Li-air cell with Ag/China carbon composite. Cell area: 1.1 cm^2 and current: 0.2 mA
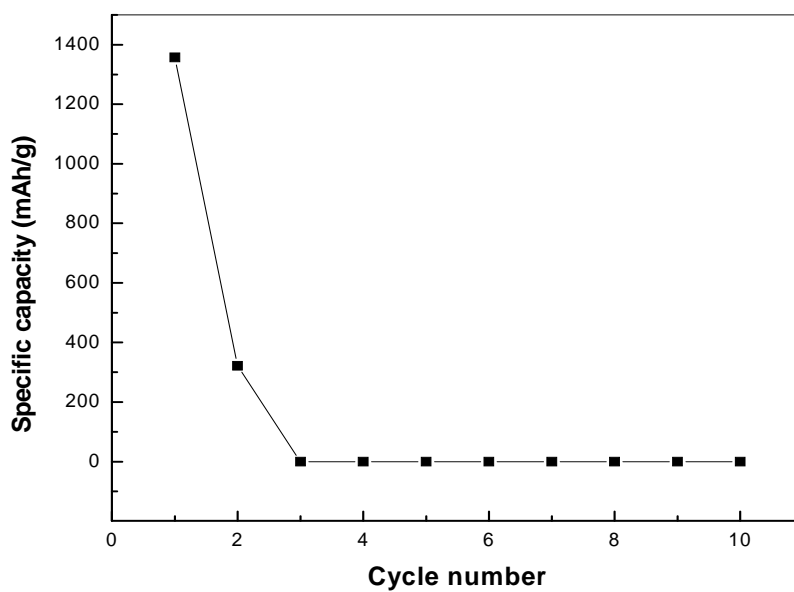
Fig 18: Variation of specific capacity with cycle number of cell assembled using TiO_2 as a catalyst on China carbon support. Cell area: 1.1 cm^2 and current: 0.2 mA
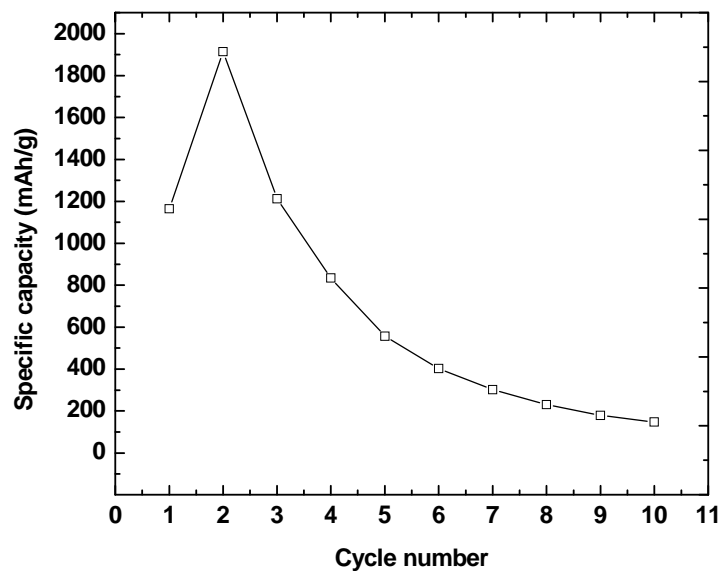
Fig 19: Specific capacity versus cycle number graph of cell assembled with electrode made using pyrogallol as a catalyst on China carbon support: Cell area: 1.1 cm^2 and current: 0.5 mA.
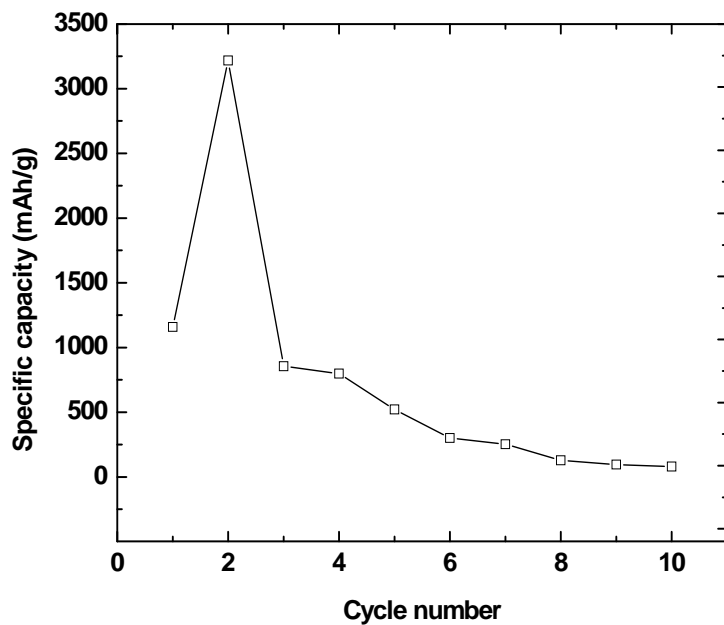
Fig 20: Specific capacity versus cycle number with benzoquinone as catalyst on China carbon support. Cell area: 1.1 cm^2 and current: 0.5 mA
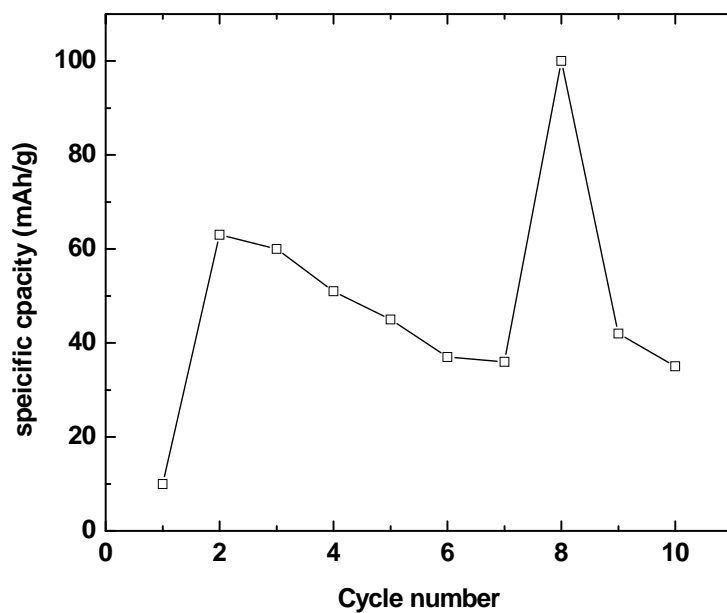
Fig 21: Variation of specific capacity of Li-air cell employing ionic liquid as a solvent. Cell area: 1.1 cm^2 and current: 0.1 mA
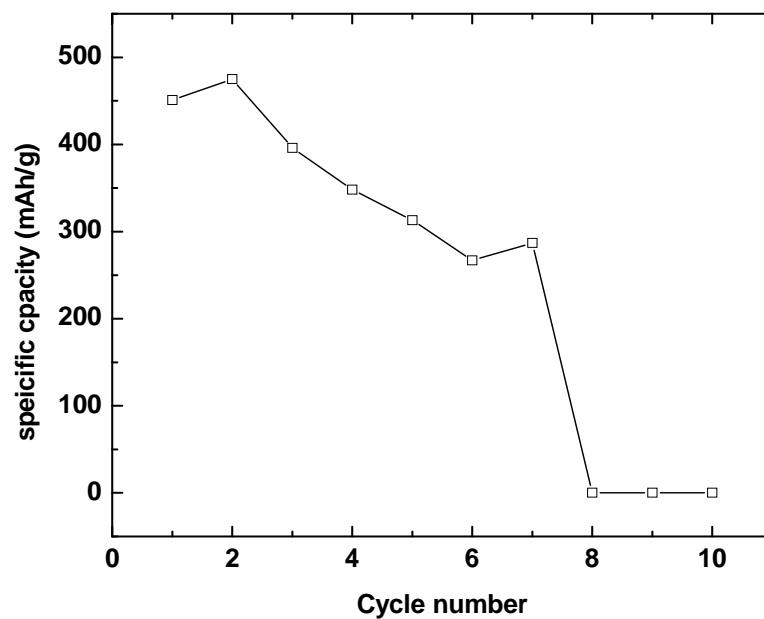
Fig 22: Variation of specific capacity of Li-air cell employing ether as a solvent. Cell area: 1.1 cm^2 and current: 0.2 mA

Lithium
Electrolyte
Porous carbon

Li^+
Li^+
Li^+
Li^+

LiO_2
Li_2O_2
Li_2O

e^- → V ← e^-

O_2
O_2
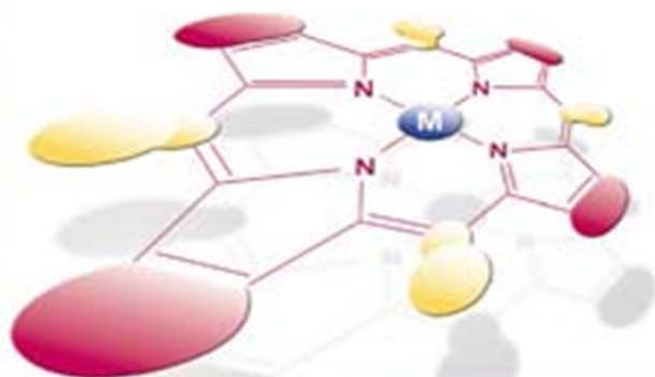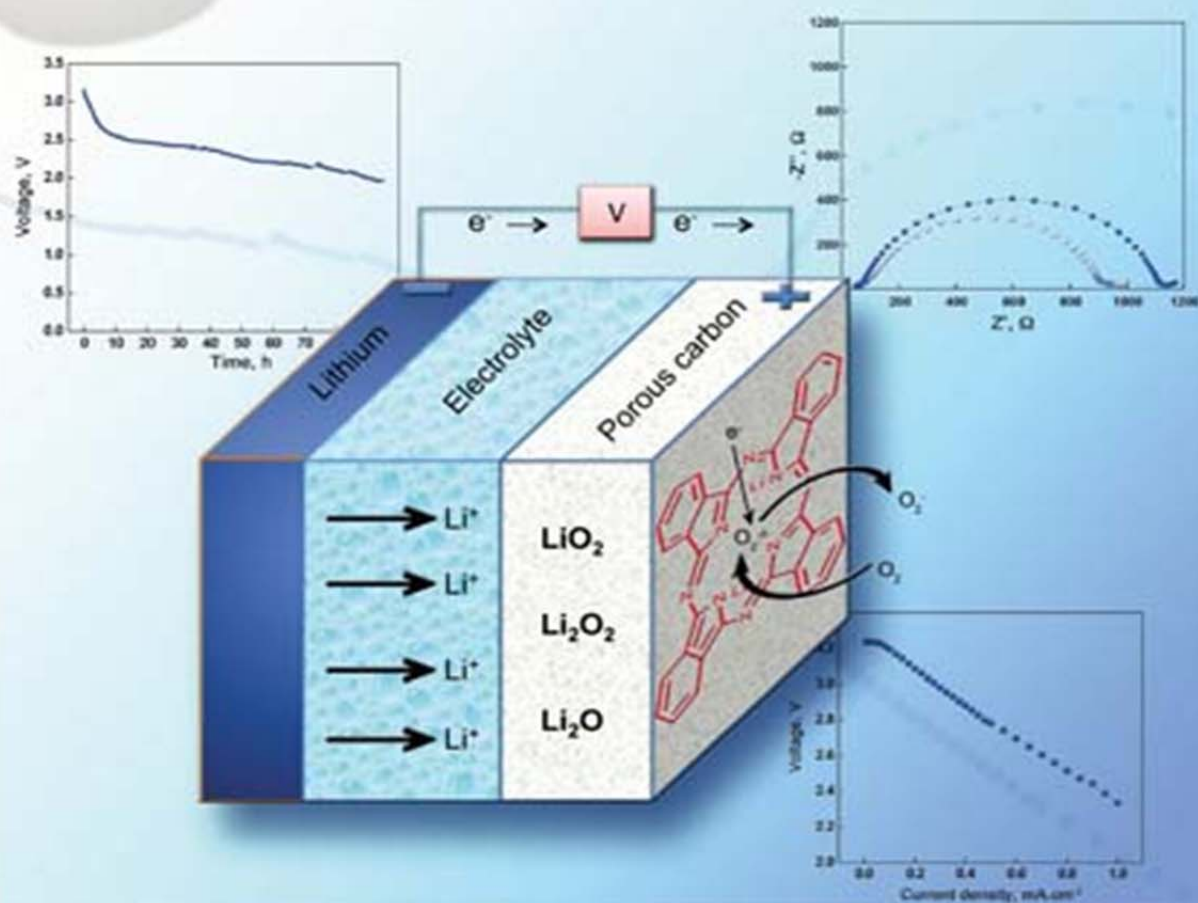
Dilithium phthalocyanine as a catalyst for oxygen reduction in non-aqueous Li-O$_2$ cells

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ABSTRACT

The electrochemical performance of Li-O$_2$ cells depends mainly on the kinetics of the cathode reaction, namely, oxygen reduction reaction in non-aqueous electrolytes. The catalyst plays an important role on the kinetics of the reaction. In the present work, dilithium phthalocyanine is used as the catalyst in the cathode of Li-O$_2$ cells. Dual-layer O$_2$ electrodes are fabricated employing a high surface area microporous carbon with Ni gauge current collector present between the two layers. Discharge capacity of Li–O$_2$ cell measured at 0.2 mA.cm^{-2} is about 30 mAh.cm^{-2}. Phthalocyanine ring is considered to interact with O$_2$ producing $Li_2Pc^{+\delta}$-$O_2^{-\delta}$ as a reaction intermediate, which facilitates the electron-transfer reaction.

KEYWORDS: dilithium phthalocyanine, catalyst, oxygen reduction, Li-O$_2$ cells

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INTRODUCTION

In recent years, research and development activities of high energy batteries have gained importance for various portable and stationary applications. In the context of a search for energy sources, which can substitute petroleum based fuels, Li-air battery appears to be attractive from a theoretical stand point. According to a calculation, energy density of Li-air battery (11680 Wh.kg^{-1}) is close to that of gasoline [1]. If the development of reliable, rechargeable Li-air battery is successful, it is expected to replace gasoline in automobiles. Utilization of oxygen present in air as the cathode material in air-breathing mode (without storing inside) is an attractive feature of Li-air battery. Thus, the cathode active material is available free of cost and it is abundant in air.

Aqueous based metal-air batteries (*cf*: Zn-air) have been known for a long time [2]. In recent years, following the report by Abraham and Jiang [3] on solid - state cell employing a solid polymer electrolyte in between a Li metal anode and carbon support for oxygen cathode, studies were extended to various electrolytes such as non aqueous liquid electrolytes [4-9], ionic liquids [10], ceramic membranes [11, 12], etc.

The kinetics of oxygen reduction reaction (ORR) during cell discharge is influenced by the catalyst. The catalyst materials reported for this reaction include transition metal oxides [13], and noble metals such as Pt, Au, Pt-Au alloy, etc [14]. Heat treated metal phthalocyanine was studied recently by Zhang et al [15]. In the present study, dilithium phthalocyanine (Li$_2$Pc) is shown to function as a catalyst for ORR. Li-O$_2$ cells are fabricated and studied for electrochemical characterization. High discharge capacity values are obtained for these cells.

RESULTS AND DISCUSSION

The electrochemical properties of the O_2-electrode depend on the properties of the carbon, the catalyst and the method of electrode fabrication. The important properties that affect the performance of carbon are its surface area and porosity. A large surface area facilitates the formation of three-phase boundary (solid-liquid-gas) with a high ratio of real area to geometric area. An appropriate porosity present in the carbon is beneficial for diffusion of oxygen and also to accommodate the reaction products. These factors lead to a high specific discharge capacity. Nitrogen adsorption-desorption isotherms and porosity data of carbon used in the present study are presented in Fig. 1. The isotherm (Fig. 1A) belongs to Type I, in which the volume N_2 adsorbed increases asymptotically and approached a limiting value. This indicates that all surface sites of the carbon sample are occupied and it consists of micropores of size not exceeding a few adsorbed molecules [16]. At high relative pressures, the pores are filled by adsorbed or condensed adsorbate molecules leading to the appearance of plateau on the isotherm. This indicates that there is no additional adsorption after the micropores are filled. The Barrett, Joyner and Halenda (BJH) curve (Fig.1B) indicates the presence of micropores of diameter less than 2 nm. The Brunauer, Emmett and Teller (BET) surface area measured from adsorption isotherm at low relative pressures is 1550 $m^2.g^{-1}$. The presence of large surface area and micro-pores in the carbon used for fabrication of O_2 electrode together with Li_2Pc as the catalyst is found to provide a high discharge capacity as detailed below.

The open-circuit voltage of the Li-O_2 cells was about 3.20 V. A cell was subjected to discharge with various magnitudes of current for about 10 min at each current and the variation

of cell voltage is shown in Fig. 2A. The cell voltage at the end of 10 minutes was used for plotting polarization curve as presented in Fig. 2B. There is a decrease in cell voltage with an increase in current. The cell voltage is 2.40 V at a current density of 1.0 mA.cm^{-2}. The reactions expected at individual electrodes during the cell discharge are as follows. Oxidation of Li takes place at the anode (reaction 1).

$$Li \longrightarrow Li^+ + e^- \tag{1}$$

It is known that the reduction of O_2 in Li^+ - ion containing non-aqueous electrolytes results in the formation of Li_2O_2 and Li_2O as stable products [19]. On the basis of a large body of electrochemical data Laoire et al., [17] proposed the following mechanism for oxygen reduction.

$$O_2 + Li^+ + e^- \longrightarrow LiO_2 \tag{2}$$

$$LiO_2 + Li^+ + e^- \longrightarrow Li_2O_2 \tag{3}$$

$$Li_2O_2 + 2Li^+ + 2\,e^- \longrightarrow Li_2O \tag{4}$$

One-electron transfer reduction of O_2 in non-aqueous electrolytes forming superoxide similar to reaction (2) is known in the literature [18, 19]. Although it was proposed that peroxide and oxide ions combine with Li^+ ions present in the electrolyte producing Li_2O_2 and Li_2O (Reaction 3 and 4) [3], a recent study [20] suggests that the reaction product is Li_2CO_3 in carbonate-based electrolytes.

The polarization of the cell is contributed by both the anode and cathode reactions. However, it is known that the oxidation of Li in non-aqueous electrolytes and also polymer electrolytes is fast and its exchange current density (i_o) is high [21, 22]. Assuming a value of 1

mA.cm^{-2} for i$_\mathbf{o}$ for reaction (1), the value of overpotential expected at room temperature is 0.026

V at a current density of 1 mA.cm^{-2}, which is calculated from Eq. (5) [23].

i = i$_\mathbf{o}$ F η / (RT)   (5)

where η is the overpotential corresponding to current density i and the other symbols have their

usual meanings. Thus the polarization of Li-O$_2$ cell, which is more than 0.6 V at 1 mA.cm^{-2} is

essentially contributed by the O$_2$ reduction reaction. This indicates slow kinetics of oxygen

reduction reaction in the non-aqueous medium.

The catalyst used for the O$_2$ electrode, namely, dilithium phthalocyanine consists of an

aromatic macrocycle with two Li$^+$ ions centrally bonded to the macrocycle [24]. Li$_2$Pc was

studied for its conductivity properties and for its possible application in solid-state lithium

batteries [25]. It is known that transition metal phthalocyanines (MPc) act as catalyst for oxygen

reduction reaction, CoPc being the first of this type studied [26]. The reversible redox property

of the central metal (M) is generally considered as the source for catalysis. Recently, heat treated

FeCuPc was employed as a catalyst by supporting it on a high surface area carbon [15]. The

catalyst loaded carbon electrode provided a greater discharge capacity and also a higher

discharge voltage than prestine carbon. In the present study, the mechanism of catalysis

involving the metal center in Li$_2$Pc for ORR is not possible. Nevertheless, it is shown recently by

Bialek and Lee that electronic charge-transfer occurs directly from Pc ring to O$_2$ molecule, when

the molecules are closely located [27]. These authors have performed a full-potential linearized

augmented plane wave (FLAPW) ab-initio studies of electronic structure of CuPc in the presence

of O$_2$. The distance between Cu in CuPc and O of O$_2$ was set at 2.0 Å with O-O bond

perpendicular to the CuPc. As O is an electron acceptor, the electronic charge-transfer occurred

from Cu to the O_2 orbitals, resulting in a decrease in net charge on Cu. In addition to Cu, all other atoms available in phthalocyanine ring lost their valence electronic charge (to the extent of about 13-15%) under the influence of O_2. Calculations revealed that the amount of charge Cu atom gains due to charge-transfer from Pc ring was smaller than what was lost from the macrocycle ring orbitals. Furthermore, the total charge on the O atom near to Cu was smaller than the charge accumulated on the other O atom. These studies led to a conclusion that there was a direct charge transfer from the p-orbitals of Pc ring to π^* - orbitals of O_2 resulting in $Pc^{+\delta}$ - $O_2^{-\delta}$ interaction [27, 28]. In the context of the above findings, it is proposed that Li_2Pc acts as a catalyst for oxygen reduction reaction.

$$Li_2Pc + O_2 \longrightarrow Li_2Pc^{+\delta} - O_2^{-\delta} \tag{6}$$

$$Li_2Pc^{+\delta} - O_2^{-\delta} + 2\ e^- \longrightarrow Li_2Pc + O_2^{2-} \tag{7}$$

$$Li_2Pc^{+\delta} - O_2^{-\delta} + 4\ e^- \longrightarrow Li_2Pc + 2\ O^{2-} \tag{8}$$

Li-O_2 cells were discharged with constant current values in the range from $0.1 - 0.5$ $mA.cm^{-2}$. The variation of cell voltage with discharge time is shown in Fig. 3A, typically for 0.3 $mA.cm^{-2}$ of discharge current. The discharge capacity obtained at a current density of 0.2 $mA.cm^{-2}$ is 30 mAh. On the basis of the mass of carbon present in the active layer of the bi-layer carbon electrode, the specific capacity becomes 4180 $mAh.g^{-1}$. Although this unit of discharge capacity is usually referred to in the literature on Li-air cells, a more appropriate unit is $mAh.cm^{-2}$. This is because of the fact that carbon is not an active material, but it only supports the electrochemical reaction. In the case of battery active materials, which undergo discharge due to changes in chemical compositions, the mass (in gram) of the active material stored in the cell is

generally used for calculation of discharge capacity in mAh.g^{-1}. In Li-O$_2$ cells, the mass of O$_2$ should be used for calculation of specific capacity of the O$_2$ electrode. Nevertheless, results are generally presented in the literature on the basis of mass of carbon, because O$_2$ is not stored in the cell. The difficulty in using the mass of carbon arises because the loading level of carbon is varied over a wide range in the literature. Beattie et al. [7] presented a plot of capacity versus mass of carbon loading. At a loading of 2 mg cm^{-2}, specific capacity of about 6000 mAh.g^{-1} was reported. There was a rapid decrease in capacity with an increase in loading of carbon and only 250 mAh.g^{-1} at 6 mg.cm^{-2} is reported. Therefore, it is advisable to report discharge capacity values of carbon-air electrodes on the basis of geometric area as mAh cm^{-2} instead of reporting as mAh g^{-1} on the basis of mass of carbon. The value of first discharge capacity obtained at a current density of 0.2 mA.cm^{-2} is 30 mAh.cm^{-2}. To ensure the catalytic activity of Li$_2$Pc for ORR, carbon electrodes were fabricated without the catalyst and Li-O$_2$ cells were assembled. Average discharge capacity of these cells obtained was about 20 mAh.cm^{-2}, against 30 mAh.cm^{-2} obtained for the cells with Li$_2$Pc in the active layer of the oxygen electrode. Cells with Li$_2$Pc, but discharged in Ar environment provided an average capacity of 4 mAh.cm^{-2}. Several Li-O$_2$ cells were subjected to discharge at different values of current and discharge capacity is shown against current density in Fig 3B. Specific discharge capacity values are provided in the units of both mAh.g^{-1} and mAh.cm^{-2} in Fig. 3B. It is observed that the discharge capacity decreases with current density as expected.

Two Li-O$_2$ cells, one cell with Li$_2$Pc and the other cell without any catalyst, were assembled under identical conditions and impedance spectra were recorded at different stages of discharge. Nyquist impedance plots before discharging the cells are typically presented in Fig. 4. Similar impedance plots were recorded after discharging the cells for about 20 h at a current

density of 0.2 mA.cm^{-2}. The diameter of the semicircle is attributed to the charge-transfer resistance of the cell, which is contributed essentially by the oxygen electrode [16]. A smaller diameter obtained for the Li-O$_2$ cell with Li$_2$Pc (Fig. 4) is due to the catalytic effect of Li$_2$Pc for ORR. Similar to this observation, it was reported by Zhang et al. [15] that the diameter of Nyquist impedance plot of Li-air cell consisting of heated FeCuPc catalyst was smaller than that of the cell made with pristine carbon.

EXPERIMENTAL

Carbon powder (YEC8) was purchased from Fuzhou Yihuan Carbon, Co., China. A Li ribbon (0.3 mm thick), propylene carbonate (PC), diethyl carbonate (DEC), dilithium phthalocyanine (Li$_2$Pc), LiPF$_6$ and PTFE suspension were purchased from Aldrich. Ni gauze (40 mesh, woven, 0.13 mm dia wire) was purchased from Alfa Aeser. It was found that Li$_2$Pc did not dissolve in the electrolyte used for the cell assembly.

Oxygen diffusing carbon electrodes were prepared on Ni gauze as the current collector as reported previously [29]. The electrode consisted of two layers of carbon with the Ni current collector sandwiched between the carbon layers. A circular (12 mm diameter) piece was punched out of a sheet of Ni gauze, etched in dilute HCl, washed with water, rinsed with acetone and dried under ambient conditions. The active carbon layer consisted of carbon, Li$_2$Pc catalyst and PTFE in the weight ratio 87.5:5.0:7.5. These three constituents were mixed thoroughly in a mortar to get a dough, which was rolled on a glass plate to form a free-standing layer. This was placed on one side of Ni gauze. The mass of carbon present in the active layer was about 10 mg. The diffusion layer consisted of carbon and PTFE in a weight ratio of 70:30, which were mixed to form a dough and then rolled into a layer. This layer is placed on the other side of the Ni

gauze. The sandwich of two carbon layers with Ni gauze in between was pressed in a die at a pressure of 50 kN for 5 min. The mass of carbon present in the diffusion layer was about 240 mg. The electrode was dried at 100 $^{\circ}$C for 6 h and transferred into an argon filled MBraun glove box model Unilab. Cells were assembled in a home-made Swagelok-type PTFE containers, similar to the cells reported by Beattie et al [7] and Zhang et al [30]. A Li disk used as the anode (12 mm diameter) was punched out of a ribbon (0.3 mm thick) and surface scraped to remove an outer layer. The electrolyte was 1.0 M $LiPF_6$ in PC + DEC (1:1). A glass mat was used as the separator and absorbent of the electrolyte. The active layer of the air-electrode was exposed to the electrolyte, and a rubber bulb filled with oxygen was connected to the diffusion-layer of the cell.

Surface area of carbon sample was measured using Micromeritics Surface Area Analyzer model 2020. The cells were discharged in a galvanostatic mode using Bitrode battery testing equipment. All experiments were carried out in an air-conditioned room at 22 ± 1 $^{\circ}$C. Current density values reported are based on geometric area of the electrode.

CONCLUSIONS

Primary Li-O_2 cells are studied by fabricating a dual layer carbon electrode using dilithium phthalocyanine as a catalyst for ORR. The carbon powder has a high specific surface and micro-porosity. Discharge capacity of 30 mAh.cm^{-2} is obtained at a current density of 0.2 mA.cm^{-2}. High discharge capacity values suggest that dilithium phthalocyanine is a good catalyst for ORR in non-aqueous electrolytes. It is proposed that the catalytic effect of Li_2Pc is due to electronic interaction between phthalocyanine ring and oxygen molecule. Ac impedance spectra of Li-O_2 cells support the catalytic effect of Li_2Pc for ORR.

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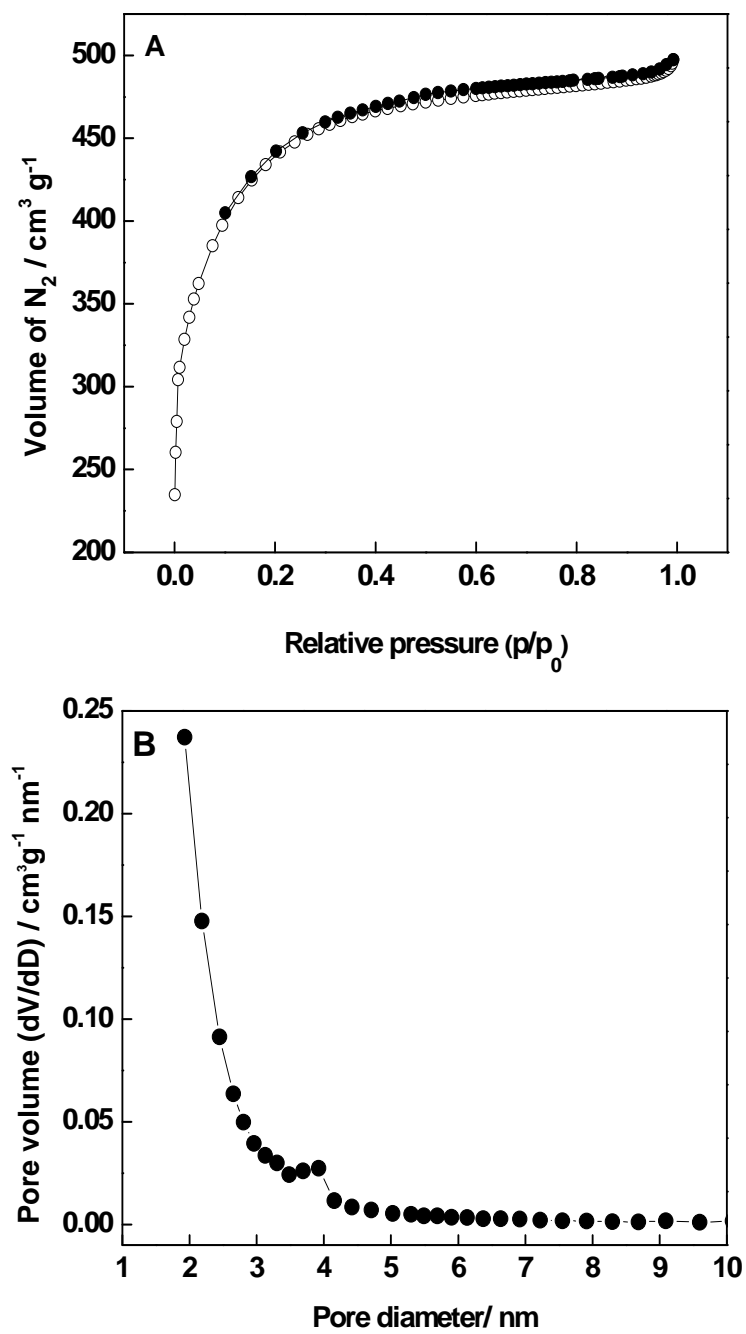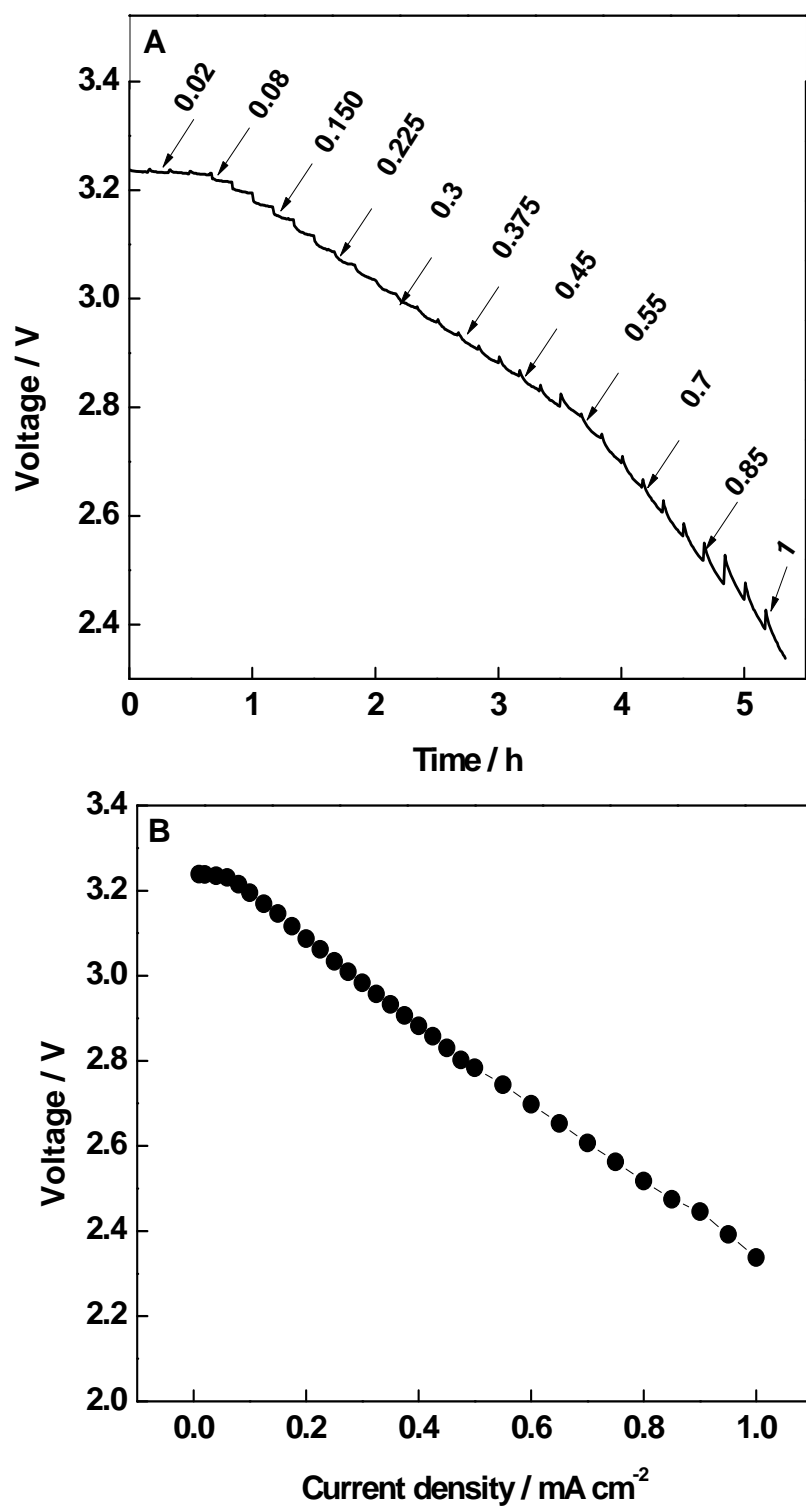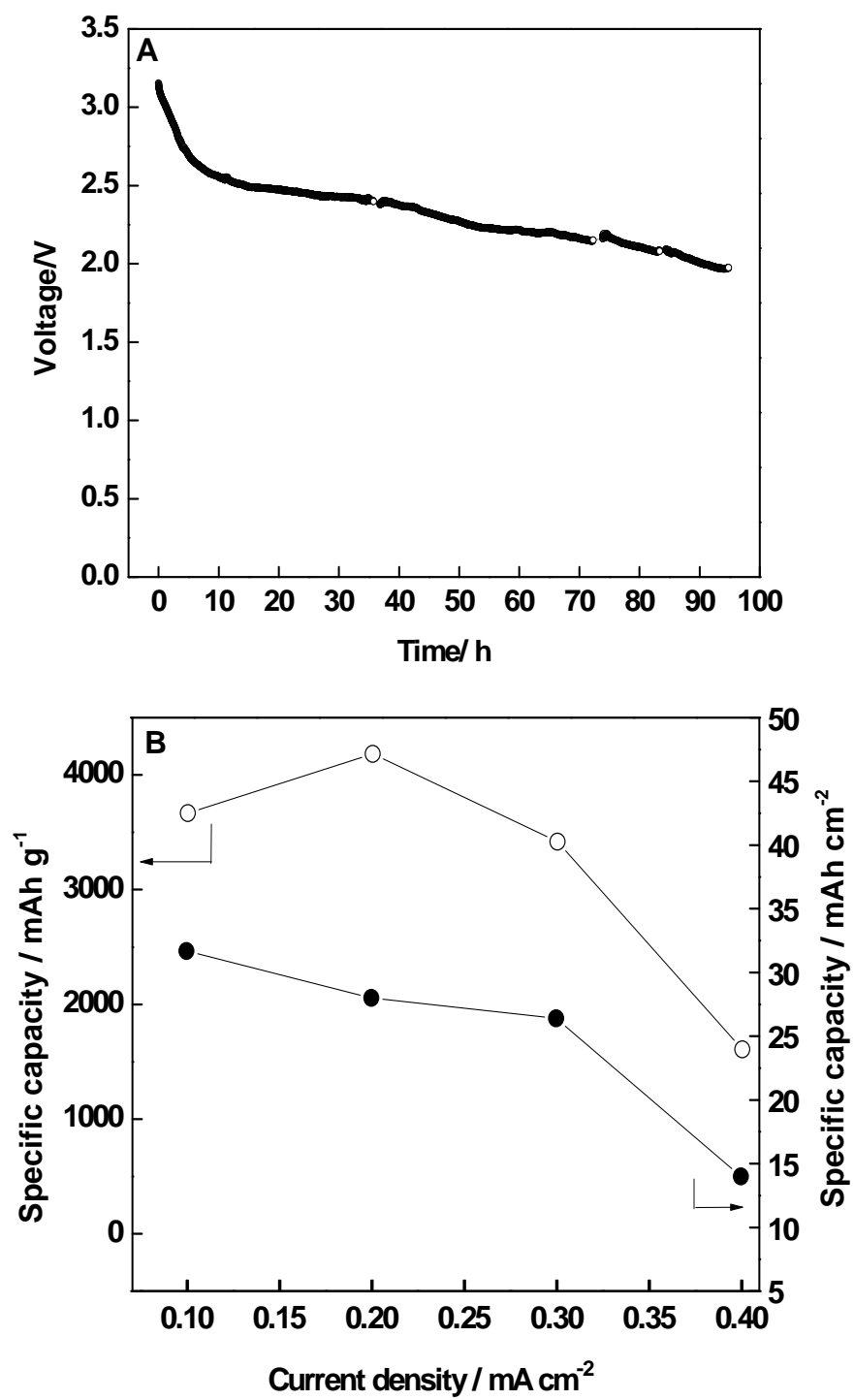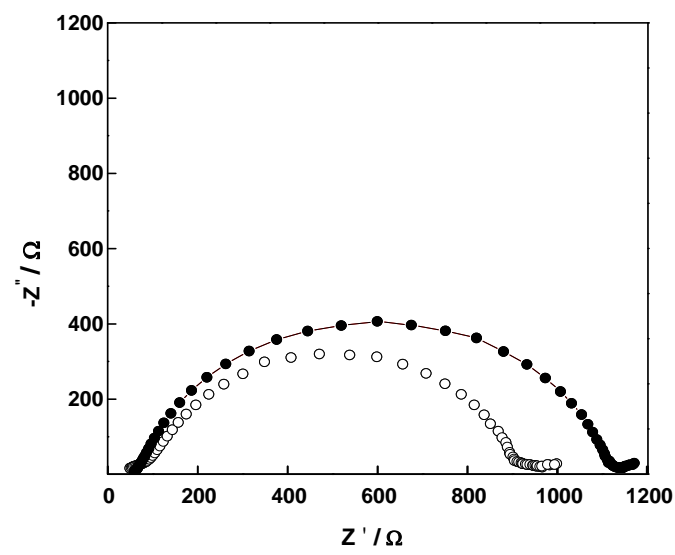
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Figure captions:

Fig. 1. (A) N_2 adsorption (○) - desorption (●) isotherm and (B) BJH pore-size distribution of carbon used for fabrication of O_2 electrode.

Fig. 2. (A) Variation of Li-O_2 cell voltage with time by varying current density (mA cm^{-2}) as indicated and (B) variation of cell voltage with current density.

Fig. 3. (A) Variation of Li-O_2 cell voltage with time of discharge at a current density of 0.3 mA cm^{-2} and (B) variation of specific discharge capacity with current density (mass of carbon present in the active layer and geometric area were used for calculation of specific capacity values).

Fig. 4. Nyquist impedance plots of Li-O_2 cells in the presence of Li$_2$Pc (○) in the carbon electrode and in the absence of Li$_2$Pc (●).